1,194,366

PATENT SPECIFICATION

1,194,366

DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Fluidized Catalyst Reactor.

We, THE STANDARD OIL COMPANY, a body corporate organized under the Laws of the State of Ohio, United States of America, of Midland Building, Cleveland, Ohio 44115, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method and an apparatus for the prevention of catalyst hold-up in a fluidised solid catalyst reactor and is concerned with the prevention of catalyst decomposition in the top portion of a fluidised, solid catalyst reactor. The invention is particularly concerned with the provision of an apparatus which substantially prevents decomposition and build-up of catalyst above the cyclone intake at the top of a fluidised solid catalyst reactor.

Fluidised, solid catalyst reactors in which a gaseous reactant component contacts a fluidised, solid catalyst, in particular in fluidised solid ammoxidation and oxidation reactors, commonly employ one or more single- or multi-stage cyclone separators to remove solid catalyst particles from the effluent gases near the top of the reactor. These cyclones, the associated piping, the duct work and the supporting members present a large amount of surface area upon which catalyst fines or dilute phase solid catalyst can accumulate. The flat, horizontal surfaces near the top of the reactor are particularly prone to accumulate substantial quantities of catalyst. The catalyst which accumulates on these surfaces, and in particular the stagnant or immobilised catalyst, tends to be chemically reduced by prolonged contact with the effluent gases and this has several undesirable consequences. The heat generated by the reduction of the catalyst and/or the reoxidation of the reduced catalyst causes the catalyst to be damaged by loss of surface area which is an important physical characteristic of the catalyst and to suffer damage in other ways. In some cases, the fine catalyst particles which accumulate at the top of the reactor become fused and agglomerated into much larger particles and even into large chunks. When the catalyst becomes fused, it often becomes sticky causing more dilute phase catalyst in its vicinity to stick to the fused surface and ultimately to suffer the same fate. As this process continues, the entire cyclone region in the top or head of the reactor may become packed with reduced and fused catalyst. Mechanical vibration causes large and small pieces of the fused catalyst in the reactor head to break loose and to fall into the dense phase catalyst bed of the reactor proper. The presence of these large pieces of catalyst in the reactor frequently disrupts the normal patterns of gas flow and catalyst circulation causing inefficiency in conversion and, in extreme cases, causing damage to the remainder of the catalyst.

The present invention substantially overcomes the problems discussed above.

The invention provides a vertical, substantially cylindrical, fluidised solid catalyst reactor internally equipped with:

(a) at least one cyclone with an inlet horn and associated piping, duct work and supports near the top of the reactor;

(b) a horizontal plate of planar configuration located immediately above the inlet horn of the cyclone or the first stage cyclone and extending substantially over the entire internal cross-sectional area of the reactor, and at least one

aperture in the plate to allow communication between the spaces above and below the plate; and

(c) a gas inlet port located in the top portion of the reactor in the region above the horizontal plate.

The invention also provides a method of operating this reactor in which the deposition, fusion and/or reduction of a fluidised solid oxidation catalyst in the region of the cyclone and its associated piping, duct work and supports above the said plate is substantially prevented by continuously feeding an inert gas through the said gas inlet port into the region above the horizontal plate.

Reference is now made to the accompanying drawing which is an axial section of the upper part of one embodiment of a vertical, substantially cylindrical, fluidised bed catalyst reactor according to the present invention. The illustrated reactor is constructed of steel or other appropriate metal and is equipped with a three-stage cyclone, each stage having a dip leg and an effluent line leading out of the reactor from the third stage of the cyclone. The reactor shell is equipped with an opening and a duct for an inert purge gas and a horizontal plate with an open area is provided immediately above the cyclone horn of the first stage. The open area in the horizontal plate can be at any location but is preferably somewhat removed from the cyclone area.

A horizontal plate of planar configuration is positioned at an elevation within the reactor immediately above the primary or first stage cyclone inlet horn. This horizontal plate extends substantially over the entire open cross-sectional area of the reactor and is fitted around dip legs, cyclone bodies and other internal members with sufficient space provided between the plate and the internal member in question to allow for thermal expansion and contraction.

A small percentage of open area is provided in the horizontal plate preferably removed from any of the cyclones, associated piping, duct work and supporting members. The exact position of this open area in the horizontal plate is not critical, provided the enclosed gas volume in the head of the reactor is in free communication with the main reactor gas stream.

In addition, an inert purge gas is bled continuously into the region above the horizontal plate at such a rate that the average linear velocity of the inert purge gas passing out through the open area in the horizontal plate into the reactor proper is in the range of from 0.1 to 10 ft/sec. The open area in the horizontal plate comprises from about 0.1% to 10% of the total cross-sectional area of the reactor. It is large enough to permit any change in pressure between the main reactor volume and the volume above the horizontal plate to equalise by feathering the inert gas flow to the stagnant zone above the plate without developing a pressure differential during the equalisation process greater than about 5 p.s.i.g.

The present invention prevents the usual deposition, stagnation, reduction and/or fusion of catalyst in the region of the reactor above the cyclone horns. Costly damage to the catalyst and ultimate shut-down of the reactor due to disruptive, fused catalyst lumps in the dense phase, fluidised catalyst bed are thus eliminated.

While the invention may be applied advantageously to all fluidised catalyst, hydrocarbon oxidation reactors with internal cyclones near the top, it is particularly advantageously applied to such reactors employed in the oxidation of olefin-ammonia mixtures to unsaturated nitriles (such as propylene-ammonia to acrylonitrile or isobutylene-ammonia to methacrylonitrile), the oxidation of olefins to aldehydes and acids (such as propylene to acrolein and acrylic acid or isobutylene to methacrolein and methacrylic acid), and the oxidative dehydrogenation of olefins to diolefins (such as butene-1 to butadiene). Especially outstanding advantages are experienced when the invention is practised with catalysts comprising the element antimony (such as antimony oxide in combination with one or more elements from the group: uranium, iron, manganese, tin, bismuth, cerium, thorium, molybdenum, tungsten, vanadium, tellurium and selenium) and particularly the catalysts disclosed in U.S. Patents Nos. 3,200,084; 3,200,081; 3,198,750; 3,197,419 and 3,244,642.

In one preferred embodiment, the invention is practised as follows:

(1) A horizontal plate ⅛″ or ½″ carbon steel is fitted over the open cross-section of the reactor at the elevation of the top of the primary cyclone horns. It is fitted around dip legs, cyclone bodies and other internals members so that the fit between the plate and any internal member which extends through the plate allows for thermal expansion and contraction.

(2) Additional holes are provided in the horizontal plate to bring the total open area (sum of gaps around members and additional holes) within the range of from 0.5% to 5% of the reactor cross-section.

(3) Provision is made to feed inert gas from an inert gas generator into the head of the reactor above the horizontal plate at such a rate that the average linear gas velocity of the inert gas passing through the open areas in the horizontal plate is within the range of from

0.3 to 1.0 ft/sec (calculated at the temperature and pressure of the reactor).

The invention is illustrated by the following example.

Example

(A) In a control reaction which is outside the scope of the present invention, acrylonitrile was prepared from a mixture of propylene, air and ammonia in the presence of an antimony oxide-uranium oxide catalyst. The reactor was a cylindrical tube constructed of steel having a diameter of 11 feet and a height of about 50 feet. The catalyst bed depth was 22 feet under static conditions and the catalyst was a fluidised solid, combined antimony oxide-uranium oxide catalyst on a silica carrier more fully described in U.S. Patent No. 3,198,750. The reactor contained perforated horizontal plates or sieve-trays spaced at two foot intervals and each of the sieve-trays had about 30% open area with $\frac{5}{8}''$ diameter holes, as more fully described in U.S. Patent No. 3,230,246. The feed consisted of propylene:air:ammonia in the mol ratio of 1:10.5 to 11.5:1.15, respectively. The reaction temperature was 920 to 940°F and an initial pressure of about 16 to 18 p.s.i.g. was reached in the upper portion of the reactor. The top of the reactor was equipped with a multiple cyclone arrangement as shown in the drawing without the horizontal plate. A feed rate of 1.5 feet per second was the superficial linear velocity. The superficial linear gas velocity is defined as:

$$\frac{\text{Volume of feed in cubic feet per second}}{\text{Reactor cross-sectional area in cubic feet}}$$

and is expressed as feet per second.

The reaction was started up and a total conversion of 90 to 95% of propylene was achieved. An initial per pass conversion of propylene to acrylonitrile of 66% to 68% was obtained. The reaction was carried out continuously for about three months. Initially, a normal catalyst loss of about 100 pounds per day was observed in the effluent and this was continuously replaced. By the end of the three months operation period, however, apparent catalyst losses were from 200 to 500 pounds per day with no more than 100 pounds per day in effluent. The per pass conversion of propylene to acrylonitrile had also dropped to the range of 60 to 63% by this time and temperatures in excess of 1000°F had developed in the top of the reactor. The operation was shut down and it was found that the region in the vicinity of the cyclones and particularly on the horizontal surfaces was completely filled with fused, reduced catalyst and that several tons of fused, reduced catalyst, which was damaged beyond use, were deposited in the cyclone region.

(B) The process of the present invention is illustrated with a repeat of (A) with the exception that the horizontal plate and inert gas inlets shown in the drawing were used with nitrogen as the inert gas at a linear gas velocity at the gas inlet of about 0.5 ft/sec. In this experiment, no more than the normal 100 pounds per day of catalyst were lost in the effluent, a normal 66 to 68% per pass conversion of propylene to acrylonitrile was achieved, no great temperature increase occurred in the top of the reactor, and no build-up of fused, reduced catalyst in the cyclone region of the reactor was observed after more than three months of continuous operation.

WHAT WE CLAIM IS:—

1. A vertical, substantially cylindrical, fluidised solid catalyst reactor internally equipped with:
(a) At least one cyclone with an inlet horn and associated piping, duct work and supports near the top of the reactor;
(b) a horizontal plate of planar configuration located immediately above the inlet horn of the cyclone or the first stage cyclone and extending substantially over the entire internal cross-sectional area of the reactor, and at least one aperture in the plate to allow communication between the spaces above and below the plate; and
(c) a gas inlet port located in the top portion of the reactor in the region above the horizontal plate.

2. A catalyst reactor according to claim 1, wherein the fit between the plate and any internal member which extends through the plate allows for thermal expansion and contraction.

3. A reactor as described in claim 1, wherein the open area in the horizontal plate is from about 0.1 to 10% of the cross-sectional area of the reactor in the vicinity of the horizontal plate.

4. A reactor as claimed in claim 1 or 2, wherein the cyclone is a multi-stage cyclone.

5. A reactor as claimed in claim 1 substantially as herein described.

6. A reactor as claimed in claim 1 substantially as herein described with reference to the accompanying drawings and/or the specific example.

7. A method of catalytic oxidation using a reactor as claimed in any of claims 1 to 6 in which the deposition, fusion and/or reduction of a fluidised solid oxidation catalyst in the region of the cyclone and its associated piping, duct work and supports above the said plate is substantially prevented by continuously feeding an inert gas through

the said gas inlet port into the region above the horizontal plate.

8. A method as claimed in claim 7, wherein the linear velocity of inert gas passing through the open area in the horizontal plate is in the range of from 0.1 to 10 feet per second and the pressure differential between the inert gas above the horizontal plate and the gases in the remainder of the reactor is not greater than about 5 p.s.i.g.

9. A method as claimed in claim 7 substantially as herein described.

10. A method as claimed in claim 7 substantially as herein described with reference to the accompanying drawing and/or the specific example.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*